

CEMENT AND LIME MANUFACTURE

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The Wet or Dry Process of Portland Cement Manufacture.

By H. ANDREWS.

THE wet process of manufacture of Portland cement has now been universally adopted in this country. The works in the principal district of the cement industry, namely, on the banks of the rivers Thames and Medway, have adopted this process for nearly a century. The raw materials used there, chalk and clay, are both soft and can be ground together by washing, which, having regard to power consumption, is the obvious method for preparing them for the manufacture. Works on the river Tyne, in the Tees and Humber districts, in Sussex, and in South Wales are also manufacturing on the wet process, although they are not all using river clay; and even the modern works in the Midlands, manufacturing from materials not excessively wet, have been designed for this process.

The raw material mix (the slurry) contains normally about 40 per cent. of water, although at some works it may be slightly less. This means that about one ton of water has to be evaporated in the kiln for each ton of clinker produced. The estimated heat required to effect this is about 2,800,000 B.Th.U.; actually even more heat will have to be expended and, expressing this in standard coal, about $2\frac{1}{2}$ cwt. will have to be burnt to produce this heat.

In dry-process works, of which one or two have been in operation in the Midlands and others are still working in America and on the Continent, the fuel consumption in the kilns is less than in wet-process works. The waste gases leave the kilns at a high temperature, but they are used for drying the raw materials or for raising steam in waste-heat boilers. This method makes use of the waste heat, but rather complicated machinery has to be provided.

A machine has in recent years been developed and is in operation in connection with rotary lime kilns for drying and heating the raw stone fed into the kilns,

and consists of a grate inclined to suit the angle of slope of the material to be dried. The material gravitates down the grate at a determined thickness, the hot waste gases are drawn through the bed by an exhaust fan, and the water in the material is thereby evaporated. The machine contains no moving parts, the material moves by gravitation, and the speed of travel is adjustable; the thickness of the bed on the grate is also adjustable to give the required effect. The grate may be of the bar or louvre type to suit the material. The diagram (Fig. 1) illustrates the arrangement, and it will be seen that the hot kiln gases do not come in contact with any metal parts; they pass through the cold material first and are thereby cooled to a temperature which is harmless to metal. The speed at which the

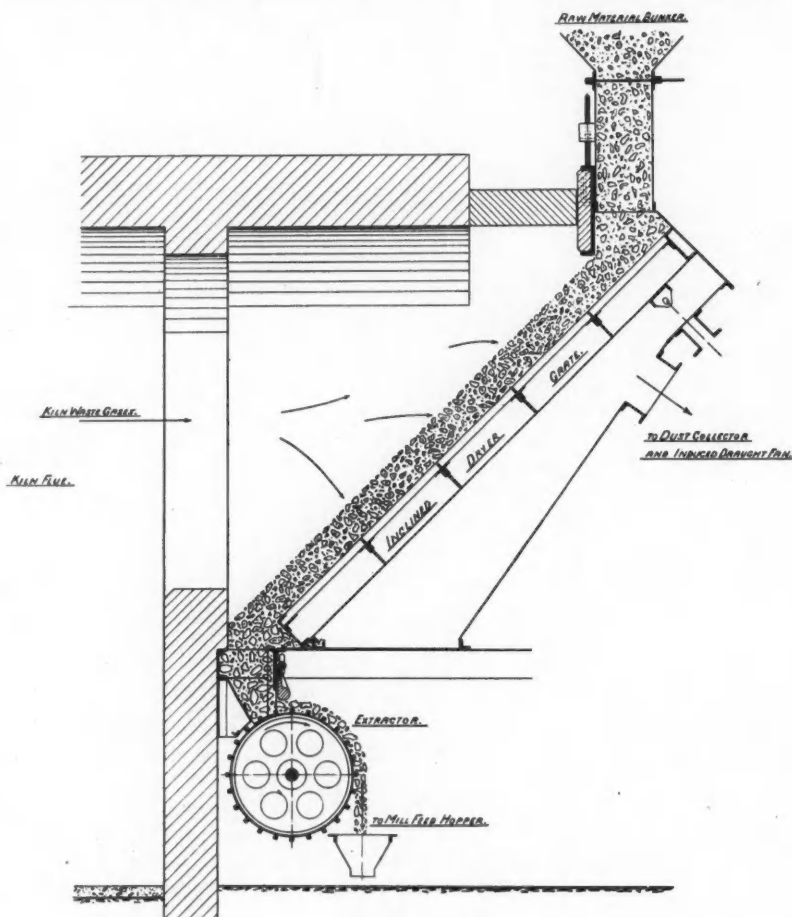


Fig. 1.

material gravitates on the grate is adjustable by the extractor, which can be rotated at variable speeds.

One grate for each raw material placed close to the feed end of a rotary cement kiln will dry the raw material without the complication of rotary dryers, etc., and, being completely enclosed, is dust-proof. The grate is not suitable for river clay containing about 40 per cent. water, but it has been used for chalk as quarried and can be used for clay with similar moisture content. In rotary lime kilns the temperature of the gases is reduced from about 1,300 deg. F. to 450 deg. F. in passing through the bed of material on the grate. It has been found that by increasing the thickness of the bed the temperature can be reduced to about 220 deg. F., but this, of course, increases the power required for driving the exhaust fan.

It may be interesting to examine typical materials in order to determine whether the heat in the waste gases from a rotary cement kiln will be sufficient to dry the raw materials. It is assumed that the kiln output is 7 tons of clinker per hour and the materials are limestone with 5 per cent. of water and clay with 20 per cent. of free moisture, the proportion of the mixture may be 4 to 1.

The dry raw meal required to produce 7 tons (15,680 lb.) of clinker is 23,800 lb. if the loss on ignition is 34 per cent.

At the proportion of mixture of 4 to 1, 19,040 lb. of dry limestone are required, and 4,760 lb. of dry clay. The water in the limestone (5 per cent.) amounts to 1,002 lb. and that in the clay (20 per cent.) is 1,190 lb., making a total of 2,192 lb. to be evaporated per hour. To effect this the following heat is required:

	B.Th.U.
(1) To heat 23,800 lb. of raw material from 50 deg. F. to 212 deg. F.— 23,800 × 0.2 (212 — 50 deg. F.)	771,120
(2) To raise the temperature of 2,192 lb. of water from 50 deg. F. to 212 deg. F.—2,192 × (212 — 50 deg. F.)	355,104
(3) To evaporate 2,192 lb. of water—2,192 × 966	2,117,472
(4) To heat 2,192 lb. of steam to the waste gas temperature of 450 deg.—2,192 × 0.48 (450 — 212 deg. F.)	250,376
Total	3,494,072

This is the total heat required to evaporate 2,192 lb. of water, and to dry the raw materials for producing 7 tons of clinker per hour. The kiln has to provide this heat.

It is assumed that the fuel burnt in the dry-process kiln to produce 7 tons of clinker amounts to 24 per cent., or 3,763 lb. The air for combustion including excess air is taken at 12 lb. per pound of coal. Thus $3,763 \times 12 = 45,156$ lb. of combustion gas leave the kiln per hour. This does not include the CO_2 from the limestone. It is also assumed that the gases leave the cement kiln and enter the material on the grates at 1,400 deg. F. After passing through the materials, the temperature of the gases is cooled to 450 deg. F.

The heat in the combustion gases containing about 75 per cent. N_2 and 25 per cent. CO_2 is about 330 B.Th.U's per pound, and that in the same gases cooled to 450 deg. F. is about 85 B.Th.U's per pound. The difference of 245 B.Th.U's per pound is available for drying. The total heat in the gases is $45,156 \times 245 = 11,063,220$ B.Th.U's, which is more than treble that required for drying. At works using chalk or marl the moisture in the calcareous material may be 20 per cent. ; the total heat required for drying is then 8,162,448 B.Th.U's, and this can still be provided by the waste gases.

The dried raw materials discharged from the grates are elevated and deposited in separate bins, from which they are extracted and measured or weighed before being fed into the grinding mill. They are thus proportioned in the dried condition, not with varying moisture as in the wet process, so that the correct composition of the raw meal is more easily maintained. The ground meal is stored in silos and may be fed into the kiln either dry or slightly moistened.

The kiln waste gases, having passed through the bed of material on the grate, are cleaned in dust collectors and discharged into the atmosphere by the induced-draught fan through a chimney. The escape of dust from the kiln in the dry process will be greatly reduced by the grates, as these have proved to act as filters retaining a large percentage of dust. From rotary lime kilns no more dust escapes than from wet-process rotary cement kilns.

In view of the present high cost of coal and the need to use as little as possible, it is hoped that these notes may be of interest in discussing this problem, which is continuously under consideration, in connection with a process which involves the evaporation of a ton of water per ton of clinker.

"Bone Meal" Made at a Cement Works.

DUE to a shortage of animal bone meal, most of which was formerly imported from South America, this product is now being made at one of the plants of the Marquette Cement Manufacturing Co., of Chicago. Pulverised animal bone is used to supplement the feed of stock and poultry, and the substitute takes the form of rock phosphate from which practically all the fluorine is removed. The process has been patented by the Davison Chemical Corporation, and results in a product with the following guaranteed analysis :

	Per cent.
Calcium (minimum)	21.2
Phosphorus (minimum)	10.9
Fluorine (maximum)	0.3
Ratio of fluorine to phosphorus (maximum)	1.4

The cement plant was readily adapted to processing the rock phosphate, the only important addition being a new installation for making acid phosphate. The raw materials for making acid phosphate are 54 deg. Baumé sulphuric acid and Florida land pebble phosphate rock. The sulphuric acid is received in tank

wagons and stored in two elevated tanks on concrete piers alongside the acidulating plant. From these tanks it runs by gravity to a two-compartment lead-lined wooden service tank, where the acid is slightly diluted with steam to 52 deg. Baumé. Steam is used for warming as well as diluting the acid. From the wood service tank the acid is pumped by one of two 3 in. rubber-lined acid pumps to a weighing tank over a pug-mill type mixer, designed to hold the mixture a certain length of time as well as to prevent it from balling.

The pebble phosphate is received dry and has the following average analysis :

	Per cent.						
P_2O_5	35.330
Al_2O_3	0.870
Fe_2O_3	0.890
Soluble (Al_2O_3)	0.800
Soluble (Fe_2O_3)	0.890
CaQ	49.620
MgO	0.140
F	3.760
SiO_2	7.400
MnO	0.033
Na_2O	0.140
K_2O	0.090
S (total as SO_3)	0.320
TiO	0.070

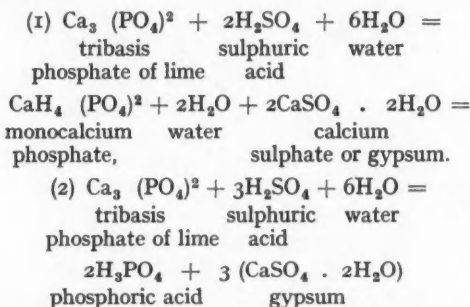
The phosphate is elevated to a storage feed bin over a mill where it is pulverised and air separated to 90 per cent. passing a 200-mesh sieve. A 4 in. Fuller-Kinyon pump elevates the pulverised material to a feed bin over the weighing batcher which serves the mixer with accurately proportioned amounts of pulverised rock and sulphuric acid (about 55 parts of rock to 45 parts of acid by weight). From the mixer the material drops into a sealed compartment below (known as a "den") where the reaction between the rock and the acid continues. The reaction produces heat, steam, acid fumes and dust, so both the mixer and den are tightly enclosed and an exhaust fan carries the dust and fumes to a stack where water sprays bring these down in solution or suspension. This liquid is wasted. It contains about one-half the fluorine in the original rock, and probably some sulphuric acid.

From the den, the acid phosphate is removed by a slow-moving pan conveyor, which discharges to an elevator feeding belt conveyor extending 300 ft. through the storage building. At the end of the pan conveyor is a revolving "knife" which breaks up the material, which, after at least three days, is in condition for further processing.

After the curing period, during which reaction is apparently continuing, the acid phosphate is loaded by a tractor scoop into dumpers, which haul the material across the yard to a hopper at the feed end of a kiln 200 ft. long by

11½ ft. in diameter. At this stage the acid phosphate contains about half the original amount, or about 1.7 per cent. of fluorine.

The raw material for the calcination process, omitting the minor compounds of iron, silica, alumina, etc., is based on the following chemical reactions in the acid phosphate plant :



The free phosphoric acid in the second equation reacts with tribasis phosphate $\text{Ca}_3(\text{PO}_4)_2$ to form the monocalcic phosphate $\text{CaH}_4(\text{PO}_4)_2$, or acid phosphate, which is the desired product for kiln feed. Before feeding to the kiln the acid phosphate is reduced to minus 1 in. size. The material goes through the kiln in small granules, and in a rather small stream for the size of the kiln, for it does not turn over like cement clinker—clinging rather closely to the kiln lining, which does not acquire a coating and hence is relatively smooth.

The kiln turns 1 r.p.m., or a little faster than when making cement clinker. The temperature is about 2,400 deg. F. In order to use pulverised coal, a small oil burner is placed under the coal burner to keep the coal ignited. The kiln is probably larger than is required for the calcination of the acid phosphate. It is operated in two 8-hour shifts per day at present, and has an output of about 10 tons per hour.

The calcined product passes through the rotary clinker cooler under the kiln, and by covered conveyors and elevators it is returned to the firing end of the kiln house, where it passes through a 30 in. by 24 in. roll pulveriser in closed circuit with two 3 ft. by 6 ft. 2-deck vibrating screens, the top decks serving merely as scalpers. The product of the rolls and screens is a white powder, minus 20-mesh, which is packed in 100 lb. paper valve bags on a standard bag packer.

The foregoing notes are from an article in "Rock Products" for July, 1944.

Burning Lime in Cement Kilns.

DUE to the completion of most of the constructional work and airfields in connection with the war, there has been a serious decline in the demand for Portland cement in the United States. At the same time there has been an increased demand for lime for chemical processes in various war industries. To meet the changed conditions, some of the American cement manufacturers have converted cement kilns to the burning of lime as a temporary wartime measure, with a view to again converting the kilns for cement manufacture after the war, when it is anticipated that there will be a great demand for Portland cement for use in constructional work that has been held up during the war. The method of conversion adopted by one company, the Manitowoc Portland Cement Co. (a subsidiary company of the Medusa Portland Cement Co.), is described at length by Mr. Bror Nordberg in a recent number of "Rock Products," from which the following notes are taken.

The mill is a wet-process plant, with three 10 ft. by 160 ft. rotary cement kilns having a rated daily capacity of 550 tons of standard Portland cement ground to a fineness of 1,650 sq. cm. per gramme.

The mill might be called a "straight-flow" plant. It is alongside and parallel to a wharf, with the raw mill building at one end and the finish mill building at the opposite end, and with the kilns in between. The raw materials are fed to the raw grinding department by a bridge crane with a $3\frac{1}{2}$ cu. yd. bucket. The crane travels parallel to the plant, over the stockpiles which are between the mill and the dock. Limestone for cement manufacture is delivered to the plant by water. This is a high-grade limestone with up to 96 per cent. CaCO_3 , which is very suitable for burning chemical lime. The only new requirement for lime is that the suppliers screen out the fines and deliver a stone from $\frac{1}{4}$ in. up to $1\frac{1}{4}$ in. or $1\frac{1}{2}$ in. in size, whereas the fines are desired for cement manufacture.

Other raw materials for the manufacture of Portland cement are shale, which is proportioned with the limestone volumetrically into the raw mill, and clay which is added in the form of slurry. Raw grinding is done in two stages, first through two kominutors (with added water) in closed circuit with two banks of three vibrating screens and then through two 7 ft. by 22 ft. tube mills in open circuit. The capacity is 25 tons per hour of which more than 97 per cent. is minus 100-mesh kiln feed material. There are five slurry tanks and two clay tanks, and the slurry, after blending and correction is pumped into kiln-feed tanks over each of the three kilns. There are three drum-type slurry filters and the slurry cake is fed into the kiln-feed spouts by belt conveyors. In recent years the practice has been to heat the slurry to 120 deg. F. by live steam in order to make filtering easier. The mill is a waste-heat plant, with three 741 h.p. waste-heat boilers, equipped with economisers. Each boiler is operated from the gases from a separate kiln. There are three separate dust chambers, and the exhaust is through a common flue to a single stack. When under full production on Portland cement the mill develops sufficient electrical power for its requirements.

Within recent years important improvements have been made to the kilns. Each has been equipped with a direct-firing bowl mill and a heat recuperator. The primary air-coal mix injected into each kiln has a temperature of about 175 deg. F. and the fineness of the coal is 93 per cent. through a 200-mesh sieve. Primary air for drying the coal as it is ground is taken from the kiln hood and tempered in each case, and the secondary air for combustion (80 per cent. of the total) enters the kilns through the recuperators.

Each kiln discharges clinker through an 8 ft. by 60 ft. rotary cooler at 180 deg. F. and, up to the time lime manufacture started, a continuous carrier placed the clinker into preliminary grinding-mill feed bins or into storage outside the finish grinding mill building. Another improvement was the installation of dust collectors above the discharge end of each kiln and the point of entry of the clinker into the rotary cooler, to draw dust from within the cooler, counter-current to the flow of clinker. Each dust collector has 30 small cyclones, and clinker dust is discharged into the clinker stream from the coolers.

Finish grinding of the clinker is accomplished through two-stage grinding. Two mills receive their feed of clinker and gypsum from bins. The clinker bins hold 50 tons each. With a 14-mesh peripheral discharge screen, the mills discharge a product of which 50 per cent. passes through a 200-mesh sieve. Finished grinding is accomplished through two 7 ft. by 22 ft. tube mills in closed circuit with a 16 ft. mechanical air separator. The finished product is pumped into silos of 50,000 tons capacity.

When the demand for Portland cement dropped off and there developed a market for high calcium lime, the problem was to adapt this plant to its manufacture without radical alterations. Production of lime started in September, 1943, and continued until January, 1944, on either one or two kilns, dependent upon the demand. No cement was manufactured during this period. In January stocks of cement had fallen to the point that it became necessary to resume its manufacture, so that No. 2 kiln produced Portland cement clinker, No. 3 kiln produced lime, and No. 1 kiln was set up to produce lime should the demand require the output of two kilns.

In producing the two products simultaneously, the raw mill grinds the cement slurry and No. 2 kiln is fed and operated as described earlier. The same bridge crane that feeds limestone and shale into the raw mill is moved to a point alongside the feed ends of the kilns to place the limestone for lime manufacture into a bin through the roof of the building. The storage bin in this case is a 240-ton capacity corrected slurry tank under No. 1 kiln, which is the standby kiln for lime manufacture.

In order to serve as a storage bin for stone, the slurry tank has been fitted with eight manually-operated draw-off bin gates through which stone is released into a 5 in. by 10 in. drag conveyor which transfers into a bucket elevator to fill a distributing hopper on the level just over the kiln-feed ends. This distributing hopper is a rectangular bin of about 10 tons capacity which has two flap gates to regulate the flow of stone into the kilns. Continuous 18 in. belt conveyors carry

the stone from either or both of the gates and discharge stone through the kiln feed spouts into the kilns—a long belt to the far kiln (No. 3) and a short one for No. 1 kiln. The flap gates, set to permit a uniform depth of stone to be carried over the belts, are fitted with electrical contact flashers which signal to the gate operator below the storage tank when the depth of stone carried over the belts is insufficient to maintain contact with the flap gate. The operator then opens the gates to release sufficient stone to maintain the level in the distributing hopper. As a further check on the quantity of stone being fed, the amount of stone carried over a 4-ft. length of belt is scooped off at regular intervals and weighed.

The kilns for burning lime rotate at the same rate and have the same lining as the one burning cement clinker. The filter cloth on the slurry filters was removed for re-installation when the kilns were reconverted to burning clinker. All the kilns are direct-fired by the unit coal mills, but the heat recuperators were removed from the kilns burning lime. The reason given for their removal is that a long, lazy flame is desired (for its effect on the quality of the lime) instead of the short intense flame used to burn cement clinker.

Whereas the secondary air to support combustion in the cement kiln is preheated through the heat recuperator, the secondary air for calcining the lime enters the kilns around the kiln hoods. Lime is burned at 2,300 deg. F. to 2,400 deg. F. and Portland cement clinker at 2,500 deg. F. Kiln No. 3 is equipped with an optical pyrometer and a continuous recording Micromax as a check on burning temperatures.

Removal of the heat recuperators was the major change required to manufacture lime, but other minor changes to the coolers and handling equipment for the finished product were necessary. In order to minimise breakage of the pebble lime, simple angle-iron lifters have been installed to replace the lifters ordinarily used in the coolers. As the lime discharges from the coolers, its temperature has been reduced to 150 deg. F. (lime cools faster than Portland cement clinker).

When production of lime was first started the plant was not calcining cement clinker and the lime discharged directly into the carrier for transfer into the finish mill feed bins which hold 50 tons each. When No. 2 kiln went into production on cement clinker in January, the grinding-mill feed bins could no longer serve for storage of pebble lime. Three steel storage bins of 600 tons total capacity were erected in the old clinker storage area outside the plant, arranged in a row so that they can be filled with lime by the carrier. Box trucks are loaded direct from the carrier stream or by means of a box truck loader, and there are draw-off gates under the three bins for removal of stored lime for loading trucks. The carrier was covered to protect the pebble quicklime from rain.

A substitute method for handling clinker from cooler No. 2 had to be devised. The 60-ft. cooler was shortened by 5 ft. to allow for the installation of a 5 in. by 10 in. drag conveyor, and a bucket elevator was installed to fill the mill feed bins. The only weakness of this handling system is that the only reserve storage of clinker now available is that stored in the mill feed bins, and it is necessary to grind one binful while the other is being filled.

Lime dust collected in the boiler hoppers is fed into the cement kiln through a dust feeder. Clinker dust from the boiler is mixed with the fresh feed in the kominutors. Clinker dust collected from the cement kiln cooler is spouted into the drag conveyor handling clinker to the grinding mill bins. Lime dust from the lime kiln coolers is returned into the carrier.

Production of lime through one kiln is 165 tons per day and the fuel ratio is 1 : 3, when burning a coal with 10 per cent. to 12 per cent. ash, 12,000 B.Th.U. that is also regularly burned in making cement. The cement kiln is producing 190 tons of clinker per day with a fuel consumption of 6 cwt. of coal per ton.

Production of lime is varied by reducing the feed of stone and coal proportionately while keeping the combustion air constant. The draught on the cement kiln is maintained at 0.2 in. of water and for lime at 0.25 in. to 0.3 in. No figures on volumes of heated gases and velocity of flow through the kilns are available.

The burning of lime is much more severe on the kiln linings than the burning of clinker, due to the fact that the kiln linings do not become coated with a protective layer. The formation of kiln rings, when burning lime, is also much more severe and it is necessary to shut down the kiln at intervals of about six weeks to remove the slag. The slag has an analysis of 85 per cent. CaO, 8 per cent. S_1O_2 , and 1 per cent. R_2O_3 , which qualifies it as a high-grade cement raw material. Accordingly, it is fed into the kominutors with fresh raw material.

Lime kiln operation has been found more efficient than cement kiln operation for waste-heat power purposes. The lime kiln gases produce more power, and the power load for grinding is much lower. The lime, of course, is not ground. Hot gases pass through the lime with less obstruction and the exhaust gases at the kiln discharge end have temperatures of 1,200 deg. F. to 1,300 deg. F., which are about 100 deg. F. higher than the gases from the cement kiln. Stack temperatures average 350 deg. F.

APPOINTMENT.—Dr. Edwin Gregory, M.Sc., M.I.E.I., F.R.I.C., has been appointed chief metallurgist of Messrs. Edgar Allen & Co., Ltd., in succession to the late Mr. S. J. Hewitt.

Dicalcium Silicate Solid Solutions.

INVESTIGATIONS on the manner of combination of Na_2O in Portland cement clinker have been made by Mr. Kenneth T. Greene (research associate of the United States National Bureau of Standards), and are reported in Research Paper No. RP1570 of the Bureau. These studies have revealed crystalline phases of chemical composition near that of $2\text{CaO} \cdot \text{SiO}_2$, but possessing properties quite different from those heretofore reported for the β form of this compound. These phases result when certain compositions in the quaternary systems $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and $\text{Na}_2\text{O}-\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ are quenched from high temperatures. Optical, thermal, and X-ray diffraction data have been obtained which indicate that they are solid solutions of Na_2O and Al_2O_3 and of Na_2O and Fe_2O_3 , in a high-temperature form of $2\text{CaO} \cdot \text{SiO}_2$ having a hexagonal structure. There is also evidence that this hexagonal lattice is the fundamental structure of the α form of $2\text{CaO} \cdot \text{SiO}_2$.

In the pure compound the α - β inversion temperature has been reported to be $1,420 \text{ deg.} \pm 2 \text{ deg. C.}$, whereas in the phases described in this paper the transformation temperature may be lowered by as much as 245 deg. C. , e.g., to $1,175 \text{ deg.} \pm 10 \text{ deg. C.}$ The inversion from α to β is accompanied by considerable ex-solution of dissolved material, showing that the extent of solid solution of these oxides in β - $2\text{CaO} \cdot \text{SiO}_2$ is much less than in the α form. As a result of this precipitation the grains of β $2\text{CaO} \cdot \text{SiO}_2$ are more or less densely clouded, closely resembling the grains of $2\text{Ca} \cdot \text{SiO}_2$ in some commercial clinkers. The data also indicate that the complex twinning structure often observed in $2\text{CaO} \cdot \text{SiO}_2$ in Portland cement clinker and in experimental preparations is the result of inversion from the α to the β phase, and is not typical of the α modification, as some investigators have believed.

Experimental Results.

The preparation that gave the sharpest powder diffraction pattern contained 90.2 per cent. of $2\text{CaO} \cdot \text{SiO}_2$, the remaining 9.8 per cent. being Na_2O and Fe_2O_3 . The oxide composition after heating was as follows:

	Per cent.
CaO	58.7
SiO_2	31.5
Fe_2O_3	5.6
Na_2O	4.2

The sample from which the X-ray pattern was made was held at $1,450 \text{ deg. C.}$ for 45 minutes and quenched in mercury. The interplanar spacings obtained from the pattern, and the values calculated for a hexagonal lattice, as suggested by Bredig's paper, are presented in Table 1.

Using the spacings with the indexes 11.0 and 00.4, the lattice constants are calculated to be $d_0 = 5.40 \text{ \AA}$ and $c_0 = 7.00 \text{ \AA}$. The axial ratio $c/a = 1.30$. The agreement between experimental and calculated values of d_{hkl} is so excellent that there seems to be no doubt of the correctness of the assumption of a hexagonal unit cell.

TABLE I.—*Powder diffraction pattern of preparation composed of $2\text{CaO} \cdot \text{SiO}_2$, Na_2O and Fe_2O_3 , quenched at $1,450^\circ \text{C}$.*

[vs = very strong; m = medium; s = strong; w = weak.]

Hexagonal indexes, hkl	Estimated intensity	d_{hkl} , experimental	d_{hkl} , calculated
10·2	vs	2·810	2·810
11·0	vs	2·700	2·700
20·1	m	2·218	2·219
20·2	s	1·945	1·946
00·4	w	1·749	1·749
12·2	m	1·579	1·578
30·0	m	1·559	1·559
11·4	m	1·470	1·471
22·0	m	1·350	1·350
13·2	w	1·217	1·216
80·4	w	1·164	1·166

A microscopical examination of this sample shows clear, slightly yellow, crystalline grains with a small amount of dark-brown interstitial glass containing quench growths of high birefringence. Some of this glass is also included in the individual grains. Between crossed nicols the interference colour of the crystalline material is a low-order grey in some fragments and in others an anomalous Berlin blue. The birefringence is probably not greater than 0·005 and the mean index of refraction is $1·713 \pm 0·003$. An interference figure suitable for a determination of the optical character could not be obtained.

When other samples of this composition were allowed to cool in the quenching furnace to various temperatures below $1,420^\circ \text{C}$. and after quenching in mercury were examined microscopically, a striking change in appearance was noted in those which had been cooled below $1,175^\circ \text{C} \pm 10^\circ \text{C}$. Above this temperature the crystalline material is clear and, with the exception of a few relatively large inclusions of glass, homogeneous. Below $1,175^\circ \text{C}$., however, the material becomes inhomogeneous, being filled with a precipitate of fine-grained brown material. This condition indicates that ex-solution of material from the solid phase has occurred. The charges cooled below the precipitation temperature also show optical properties for the matrix that differ from those of the high-temperature quenches. Samples cooled slowly to $1,150^\circ \text{C}$. show higher indexes of refraction and a higher birefringence than the clear phase stable above $1,175^\circ \text{C}$. These properties suggest β - $2\text{CaO} \cdot \text{SiO}_2$, and its presence was verified by an X-ray diffraction pattern of a charge which was heated to $1,450^\circ \text{C}$. and cooled to $1,150^\circ \text{C}$. at an average rate of about 23 degrees per minute. No lines of the hexagonal form are evident, and it is apparent that a discontinuous change in crystal structure has taken place. There seems to be little doubt that ex-solution of the Na_2O and Fe_2O_3 from the high-temperature form occurred during transition to the β modification. There may also be some remaining solid solution of these oxides in β - $2\text{CaO} \cdot \text{SiO}_2$, but it is apparently much less.

The results obtained with certain compositions in the quaternary system $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ are analogous in most respects to those in the $\text{Na}_2\text{O}-\text{CaO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ system. The best diffraction pattern resulted from quenching at 1,500 deg. C., a charge that had the following composition after having been heated :

	Per cent.
CaO	62.1
SiO ₂	31.3
Al ₂ O ₃	3.8
Na ₂ O	2.8

This represents 89.8 per cent. of $2\text{CaO}.\text{SiO}_2$, an excess of 3.6 per cent. of CaO, the balance being Na_2O and Al_2O_3 . When a hexagonal structure is assumed for this material, and the theoretical interplanar spacings calculated as in the preceding section, the agreement with experimental values is quite satisfactory, although not as close as in the case of the material containing Fe_2O_3 . This is explained by the fact that the pattern itself is less distinct. Two of the lines given in Table 1 have corresponding lines too weak to measure on this film. The data are given in Table 2. The lattice constants in this case are $a_0 = 5.44$ Å and $c_0 = 7.02$ Å. These are slightly greater than for the iron-bearing phase, although the ratio c/a is nearly the same, 1.29.

TABLE 2.—*Powder diffraction pattern of preparation composed of $2\text{CaO}.\text{SiO}_2$, Na_2O and Al_2O_3 quenched at 1,500 deg. C.*

[vs = very strong ; m = medium ; s = strong ; w = weak ; vw = very weak.]

Hexagonal indexes, hkl	Estimated intensity	d_{hkl} , experimental	d_{hkl} , calculated
10.2	vs	2.81	2.81
11.0	vs	2.71	2.71
20.1	m	2.238	2.233
20.2	s	1.955	1.955
00.4	—	—	1.755
12.2	m	1.588	1.588
30.0	m	1.569	1.570
11.4	w	1.469	1.474
22.0	m	1.361	1.361
13.2	vw	1.226	1.224
30.4	—	—	1.170

Under the microscope the grains are for the most part clear and of irregular shape. The birefringence is rather low, and is estimated to be about 0.01. The optical character is positive, and uniaxial or biaxial, with a very small axial angle. It is believed that strain brought about by quenching may be the cause of the apparent biaxiality observed in some fragments. The indexes of refraction as measured in immersion oils are $\omega = 1.702 \pm 0.003$, $\epsilon = 1.712 \pm 0.003$.

Upon subjection to slow cooling and quenching at different temperatures, this material was found to undergo a transition analogous to that described for

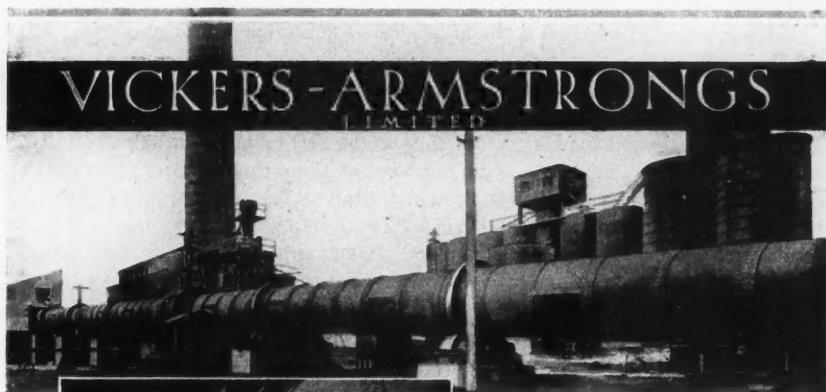
the material containing Fe_2O_3 . Below $1,180^\circ\text{C} \pm 10^\circ$, the transformation from the high-temperature form seems to be complete. The diffraction pattern of a sample heated to $1,450^\circ\text{C}$. and cooled to $1,150^\circ\text{C}$. at about 19° per minute corresponds to that of $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$. Here again the microscope reveals inhomogeneity, indicating that precipitation from solid solution has occurred. Also prominent in the grains is a complex twinning structure comprising several sets of parallel laths intersecting at acute angles. The birefringence is somewhat increased and the indexes of refraction are greater than in the higher-temperature form.

In the course of the cooling experiments on this material, it was noticed that charges quenched from certain temperatures somewhat above $1,180^\circ\text{C}$. had an appearance not entirely like that described in either of the two previous cases. A sample composed of $2\text{CaO}\cdot\text{SiO}_2$, Na_2O , and Al_2O_3 , quenched at $1,200^\circ\text{C}$. after being cooled from $1,450^\circ\text{C}$. at approximately 17° per minute, appears to represent an intermediate state in which narrow blades of $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ have formed within the residual high-temperature solid solution. Minute inclusions resulting from rapid ex-solution are not present in this quenched charge. The blade-like forms have a higher index of refraction than the crystalline material which they penetrate, and also a greater birefringence. The diffraction pattern of this sample contains lines of $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ as well as of the higher-temperature solid solution, and it is apparently a composite pattern. Although it is possible that the blades of $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ may be strictly quench growths, the appearance suggests rather that they were in equilibrium with the matrix at the quenching temperature. Such a condition is possible in a type of system where the extent of solid solution is unequal in two crystalline phases of the same substance. Certain compositions will exhibit an inversion interval over which both of the forms exist in equilibrium, but in varying proportions. If such is true in this instance, the temperature $1,180^\circ\text{C}$. represents the lower limit of the inversion interval for this particular composition.

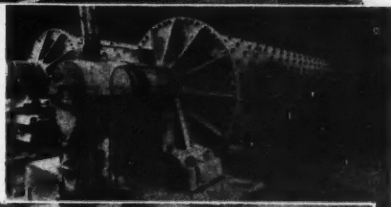
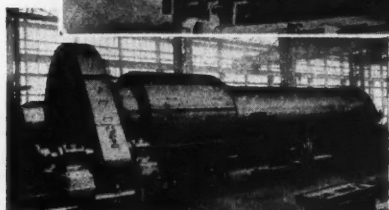
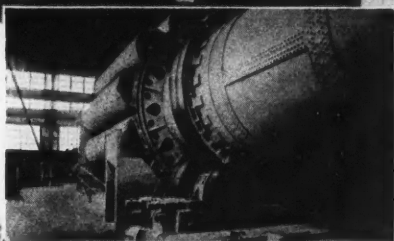
Just why a similar inversion temperature-interval was not observed in the charges containing Fe_2O_3 is not clear, unless the over-all percentages of Na_2O - and Fe_2O_3 exceed the limiting amounts that can be taken up by the $2\text{CaO}\cdot\text{SiO}_2$. In such a case the transformation from the hexagonal to the β form takes place completely, under equilibrium conditions, at a temperature corresponding to the lower limit of the interval. This conclusion is supported by the fact that considerable glass was observed in the $\text{Na}_2\text{O}\text{-Fe}_2\text{O}_3$, but very little in the $\text{Na}_2\text{O}\text{-Al}_2\text{O}_3$ charges, and may also explain why the intricate twinning of the $2\text{CaO}\cdot\text{SiO}_2$ is much more distinct in one case than in the other.

Discussion.

The foregoing data seem to demonstrate the existence at high temperatures of solid solutions composed chiefly of $2\text{CaO}\cdot\text{Si}_2\text{O}$, possessing hexagonal crystal structures. Furthermore, it seems reasonable to conclude that this hexagonal type of structure is fundamentally that of the α form of $2\text{CaO}\cdot\text{SiO}_2$, since it has been shown to invert directly to the β form upon cooling.



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The postulation of an α form of $2\text{CaO} \cdot \text{SiO}_2$ unstable at room temperature provides an explanation for the practically identical optical properties and diffraction pattern given for the α and β forms. The only usable distinguishing feature of α - $2\text{CaO} \cdot \text{SiO}_2$ has been considered to be an intricate twinning structure. It has been suggested by Insley that the complex twinning so often observed in grains of $2\text{CaO} \cdot \text{SiO}_2$ indicates that they have at some time been in the α state, rather than that they are at present in that state. The results reported in this paper tend to substantiate this belief. The complicated twinning probably results from the transition to the β phase, and it appears that the transition is accompanied by precipitation of much of the material which was in solid solution in the α phase. This precipitation is not to be confused with the formation of prismatic β - $2\text{CaO} \cdot \text{SiO}_2$, which takes place continuously over a temperature interval. From all indications, the fine-grained precipitate is produced suddenly at the temperature below which the hexagonal α structure is unstable, in this case $1,180^\circ \text{C}$.

When $2\text{CaO} \cdot \text{SiO}_2$ in Portland cement clinker is examined microscopically, it often exhibits an optical character that is nearly uniaxial. If the internal crystal structure of this phase is shown by X-ray studies to be basically that of a uniaxial crystal, then the presence in commercial clinker of hexagonal α - $2\text{CaO} \cdot \text{SiO}_2$ would be definitely indicated. If, however, the structure should be shown to be fundamentally biaxial, it would merely mean that the optic axial angle is nearly zero. Since the X-ray diffraction pattern of β - $2\text{CaO} \cdot \text{SiO}_2$ indicates that its symmetry is that of a biaxial crystal, an investigation of clinkers of recent manufacture would doubtless give a definite answer to the question of whether the phase observed is actually α - $2\text{CaO} \cdot \text{SiO}_2$ or β - $2\text{CaO} \cdot \text{SiO}_2$ with a small optic axial angle. That β - $2\text{CaO} \cdot \text{SiO}_2$ can exhibit a very small axial angle was shown by Hansen. Since this was in disagreement with Rankin and Wright, who reported large angles for both α - and β - $2\text{CaO} \cdot \text{SiO}_2$, Hansen concluded that "the size of the optic axial angle alone is not a safe criterion to use in identifying a crystalline phase in such mixtures as Portland cement."

It must be borne in mind that the greater the purity of $2\text{CaO} \cdot \text{SiO}_2$, the higher is the α - β inversion temperature, approaching as a limit $1,420^\circ \text{C}$. With increased purity there is an increased difficulty in retaining the α form at room temperature. Thus the rate of cooling must be correspondingly greater in order to prevent inversion. How rapid this cooling must be is indicated by experiments on the compositions given in this paper. Charges of less than a gramme were found to require quenching in mercury to ensure complete retention of the α solid solutions. Air-cooling by lifting the charges from the furnace was not sufficient, and resulted in a partial inversion of the phases. Commercial clinker certainly cools more slowly than these small laboratory charges. Furthermore, the alkali content of clinker is considerably lower than that of these experimental preparations. Therefore it is probable that in Portland cement clinker and in most laboratory preparations the conditions of composition and of cooling have not been favourable for the preservation of the α - $2\text{CaO} \cdot \text{SiO}_2$ solid solutions which exist at high temperatures.

From the present investigation it appears that a considerably greater percentage of Na_2O than is customarily found in commercial clinker is necessary to ensure the retention of the $\alpha\text{-}2\text{CaO}\cdot\text{SiO}_2$ structure under prevailing rates of cooling. Although the ratio of Na_2O to calculated $2\text{CaO}\cdot\text{SiO}_2$ may be appreciable in some clinkers, experimental results indicate that aside from the cooling rate the retention of the α form does not depend upon this ratio as much as upon the overall concentration of Na_2O in the mixture. However, these results do not preclude the preservation of $\alpha\text{-}2\text{CaO}\cdot\text{SiO}_2$ in Portland cement clinker by components other than Na_2O . It may possibly be found that the combined effect of minor oxides, such as the alkalis, P_2O_5 , TiO_2 , and FeO , is sufficient to bring this about under conditions of quick cooling.

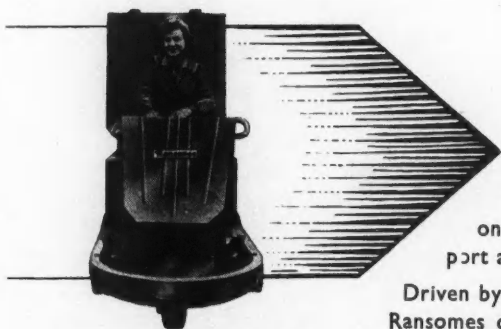
The percentages of Na_2O reported as present, after heating in the preparations described, were determined by chemical analysis. However, it is not known how much Na_2O actually enters the crystal lattice in either of the two solid solution phases. It is quite certain that both Na_2O and Fe_2O_3 in the one case, and Na_2O and Al_2O_3 in the other, enter into the high-temperature form of $2\text{CaO}\cdot\text{SiO}_2$, but the ratios in which they are taken up are not easily determined. The inclusions resulting from precipitation are very fine-grained and are surrounded by the crystalline matrix, so that analysis by optical means is extremely difficult.

There is evidence that oxides and combinations of oxides other than those for which data are given may pass into solid solution in $\alpha\text{-}2\text{CaO}\cdot\text{SiO}_2$. Preliminary experiments show that K_2O and Fe_2O_3 added in certain proportions will preserve the α structure, and it is probable, though not certain, that K_2O and Al_2O_3 can accomplish the same result. Completely twinned grains of $2\text{CaO}\cdot\text{SiO}_2$ have been observed in the system $\text{Na}_2\text{O}\text{-CaO}\text{-SiO}_2$ by the writer and also by Taylor. These grains give the diffraction pattern of $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$, but the writer believes that at high temperatures they were in the α state and that there existed at least a small amount of solid solution. Apparently the inversion cannot be prevented by quenching with only these three components present. The degree of solid solution which may occur in $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ is also of importance in the study of the oxide systems of cement. The data presented show that for the compositions investigated, at least, this solid solution is much less than in the higher-temperature, or α form. The exact amount in any particular case is difficult to determine, but quenching experiments with examination for glass have indicated that in the system $\text{Na}_2\text{O}\text{-CaO}\text{-Al}_2\text{O}_3\text{-SiO}_2$ it is very small, probably less than 2 per cent. of Na_2O and Al_2O_3 combined. A slight lowering of the indexes of refraction of $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ has been observed, and seems to be due largely to the influence of the Na_2O . X-ray diffraction patterns have shown small shifts in some of the lines, but scarcely more than the variation to be expected from experimental error.

The industrial significance of the information presented lies mainly in the value which it may have in better understanding the structure of Portland cement clinker. Investigators have recognised that $2\text{CaO}\cdot\text{SiO}_2$ varies in appearance and properties in different clinkers, and even in different samples of the same clinker. Classifications of the $2\text{CaO}\cdot\text{SiO}_2$ into types have been made on the basis of its

microscopic appearance in polished and etched specimens of clinker. The formation of these types is dependent, among other factors, upon the conditions of heating and cooling, as well as upon the chemical composition, and it is reasonable to expect that future studies on the structure of clinker will result in the correlation of the data concerning the observed types of $2\text{CaO} \cdot \text{SiO}_2$ with the solid solution and α - β inversion relationships as determined on laboratory preparations.

It is also possible that these results may help to explain the greater difficulty of bringing about the combination of CaO with the other components in clinkers high in alkalis. If $2\text{CaO} \cdot \text{SiO}_2$ solid solutions containing Na_2O or K_2O are formed in clinker, the tendency to react with CaO to produce $3\text{CaO} \cdot \text{SiO}_2$ may be considerably affected. It is possible that the α form of $2\text{CaO} \cdot \text{SiO}_2$ may behave quite differently from the β as regards its reactivity with CaO , just as β - and γ - $2\text{CaO} \cdot \text{SiO}_2$ have different rates of hydration. So far there are no experimental data on this point.



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